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Cellulosic pulp.

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Carbon dioxide in the gaseous phase is introduced through an injection assembly 25 into an alkaline delignified cellulosic pulp under conditions to adjust and maintain at from about 8.5 to 6.5 the pH of the pulp stream prior to introduction into a pulp refiner where it is fibrillated. Gaseous carbon dioxide is also introduced into the fibrillated pulp by means of an injection assembly 60 so as to maintain the pH of the pulp between 7.0 and 5.5 upstream of a paper making machine 10.

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## CELLULOSIC PULP

This invention relates to the preparation of cellulosic pulps, and more particularly to the chemical treatment of alkaline cellulosic pulp prior to processing in a paper making assembly.

At the present time the digestion of cellulosic materials is primarily carried out utilizing either soda, sulfate, sulfite or neutral sulfite processes and is sometimes performed by batch methods, i.e., particulate cellulosic materials in relatively small pieces or chips and delignifying chemicals in aqueous solution are introduced into a pressure cooker or digester wherein the mixture is raised to delignifying temperatures and thereafter discharged as concentrated pulp and spent liquor for further processing operations. Continuous methods are also known. Processing data for determining delignifying conditions, such as strength of the chemicals, time and temperature, are determined to a great extent from actual experience rather than from correlated laboratory data, since the severity of the chemical attack on the charged cellulosic materials varies considerably even within wood species.

The delignified cellulosic material from the digester is introduced into a blow tank for dilution with diluting liquors to a pumpable consistency of from 1.5 to 4 percent solids for the separation and recovery of the cooking chemicals and prior to refining and further treatment of the cellulosic pulp slurry for introduction to a paper making machine, such as a Fourdrinier machine.

To impart appropriate and/or desired physical properties to the paper, paper board or the like to be formed in such machine, diverse chemicals are added to the cellulosic pulp slurry to improve one or more properties which would be otherwise lacking. For example, sizing agents are employed to make papers resistant to penetration of certain liquids; clays and other pigments to improve brightness, opacity, and printing properties; starches and gums to improve fiber bonding and fiber distribution; various synthetic polymers to impart wet strength; dyes and colored pigments to give desired color; surface active agents to improve absorbency, combat self-sizing, and decrease foam and pitch troubles.

Generally, cellulosic pulp slurries are advantageously processed with such additives at a pH of from about 4.5 to 7.0. Cellulosic pulps produced by alkaline pulping techniques are at a pH of from about 12.0 to 10.0 and require extensive chemical treatment, e.g., a first treatment with sulfuric acid, to bring the resulting cellulosic pulp into the appropriate pH range of from 9.5 to 7.5 for effective

treatment with such hereinbefore described additives. There is thus a need for an improved process and apparatus for adjusting the pH of alkaline cellulose pulp prior to forming paper therefrom, and the invention aims at meeting this need.

In accordance with the invention, carbon dioxide is introduced in the gaseous phase into an alkaline cellulosic pulp under conditions to adjust and maintain at from about 8.5 to 6.5, the pH of the pulp stream prior to introduction into a pulp refiner. A pH of greater than about 8.5 provides minimal benefits and a pH of less than about 6.5 requires excessive carbon dioxide. A pH in the range 8.5 to 7.5 is preferred. Preferably, gaseous carbon dioxide is also introduced into the refined pulp under conditions to adjust and maintain at from about 7.0 to 5.5 the pH of the pulp stream prior to introduction into a paper making assembly. A pH in the range of 6.0 to 5.5 is more preferred.

The invention makes possible the manufacture of paper of improved physical properties. The invention also makes possible better pulp drainage thereby permitting paper forming with reduced energy requirements, for drying. Other advantages that may be derived from the use of the invention include improved operation of the paper making machine, a reduction in rejected paper, and reduced requirements for certain chemical additives (e.g. alum or aluminium sulphate).

The present invention will now be described by way of example with reference to the accompanying drawing of a schematic flow diagram of a paper making apparatus.

Referring now to the drawings, there is schematically illustrated a paper making machine, such as a Fourdrinier machine, generally indicated as 10 and including a headbox 12 for distributing paper-forming pulp stock onto the moving screen 36 of the Fourdrinier machine 10. Cellulosic pulp material produced by standard alkaline pulping techniques are introduced into a blow tank (not shown), washed and stored in a chest 14 and combined with white water in line 16 to a pumpable consistency of about 1.5 to 5.0 percent, generally about 4 percent solids, and passed in line 18 to the suction side of a pump 20.

A pulp slurry in line 22 from the discharge side of the pump 20 is contacted with gaseous carbon dioxide from line 21 by an injection assembly 25 to form a combined stream in line 26. Gaseous carbon dioxide is added in an amount sufficient to provide a pH of from about 8.5 to about 6.5, in the combined pulp stream which is passed through a refiner 28 to fibrillate the cellulosic pulp material.

In a preferred embodiment, the line 30 down-

stream from the refiner 28 contains a second injecting assembly 60 for contacting the refined pulp stream with additional gaseous carbon dioxide from line 21. Gaseous carbon dioxide is added in an amount sufficient to provide a combined stream in downstream line 62 having a pH in the range from about 7.0 to 5.5.

The pulp from line 62 is mixed with white water in line 46 to a solids consistency of about 0.4 percent and passed through pump 32 and line 34 to a headbox 12. Generally, a sizing precursor, such as alum, is added to the pulp by an alum introduction means 48. The alum may be introduced as a liquid into line 30, line 46 or directly into the headbox 12 (as shown). The pulp in headbox 12 is distributed onto the endless woven-wire belt 36 of the Fourdrinier machine 10. During passage over the endless woven-wire belt 36, a liquid (hereinafter referred to as "white water") is drained from the cellulosic pulp sheet being formed, and the pulp sheet is dried and passed to further processing steps in the formation of finished paper, generally in the form of a roll.

The white water 40 drained from the cellulosic pulp during distribution on the endless woven-wire belt 36 is collected in a sump 38 of the Fourdrinier machine 10 and is passed to a mixing tank 42, called a wire pit, to which are added by line 44 other additive chemicals as required for manufacturing a specific paper product. A purge stream of the white water is generally continually withdrawn through line 45 to maintain chemicals, such as sulfate ions, at certain predetermined levels in the recycling white water stream in line 46.

Typically, the gaseous carbon dioxide in line 21 is at a pressure of about 40 to 200 psig, and is preferably at a pressure of from 10 to 20 psi greater than the pressure of the cellulosic pulp in line 22. The gaseous carbon dioxide injection assembly 25 is a porous metal sparger, preferably, in combination with a static mixer which provides good gas dispersion and maximum transfer efficiency. Suitable spargers and static mixers are commercially available from a number of manufacturers. Proper addition of the gaseous carbon dioxide permits rapid and intimate mixing in the cellulosic pulp such that a uniform, predetermined resulting pH level is readily attained in line 26 at a point downstream of the discharge side of the pump 20 and prior to introduction into a subsequent unit operation, e.g., the refiner 28. The pH of the treated pulp slurry is measured with a meter assembly 50 having a pH probe 52 in line 26. Preferably a meter output is used to generate a feedback control signal to operate a valve 56 in line 21 to regulate the flow of carbon dioxide in line 24 to achieve the desired pH level in the pulp stream. Line 24 also contains a check valve 27.

The second gaseous carbon dioxide injecting assembly 60 is a porous metal sparger; adequate mixing may be obtained without a second static mixer. A second meter assembly 64 having a pH probe 66 in line 62 measures the pH and provides a control signal to operate a second valve 68 connected in line 70 between carbon dioxide line 21 and the second injecting assembly 80. Line 70 also contains a check valve 72. The pressure of carbon dioxide in line 21 is preferably at a pressure of from about 10 to 20 psig greater than the pressure of the refined pulp stream in line 30.

## EXAMPLES

The following examples are illustrative of conditions for the process of the present invention, and it is to be understood that the scope of the invention is not to be limited thereby.

### Example I

In a plant producing 800 tons per day of paper, a concentrated pulp stream of a pH of 11.0 and a density of 15 percent solids produced by kraft processing of soft wood, is diluted with white water to a consistency of 4 to 5 percent solids and a resulting pH of 10.5. The diluted pulp stream is introduced into and passed (with trim dilution, as required) to the suction side of a pulp pump 20 at a rate of 2100 GPM. To the dilute pulp stream in the downstream conduit from the pulp pump, there is added gaseous carbon dioxide at a rate of 7.5 pounds per minute to form a dilute pulp stream having a pH of 7.0 when introduced into a refiner 28 for processing. No carbon dioxide is added to the refined pulp stream.

Alum is added to the refined pulp stream at a rate of 10.4 pounds per minute. The thus treated refined pulp stream is thereupon further diluted with white water to a solids content of 0.4 percent and a pH of about 4.5 before introduction into the headbox 12 of the Fourdrinier machine 10 for processing into paper.

The controlled introduction of carbon dioxide before the refining step results in stronger paper as a result of improved refining when compared to the introduction of sulfuric acid to adjust pH prior to the refining step.

### Example II

In a plant producing 1500 tons per day of paper board, dilute pulp streams of a solids content of about 4 to 5 percent solids are produced by

kraft pulp processing from hard and soft woods. A dilute soft wood pulp stream and a dilute hard wood pulp are combined to form a primary line pulp stream to be refined to form the dilute pulp stream to be diluted by white water to a solids content of about 0.4 percent for introduction into the primary headbox of the paper machine.

The dilute soft wood pulp stream having a solids content of 4 to 5 percent and a pH of 10.5 is passed (including trim white water) to the suction side of a pulp pump at a rate of 3000 GPM. To the dilute pulp stream (solids content 4 percent) in the downstream conduit from the pulp pump, there is added 10.4 pounds per minute of gaseous carbon dioxide. The resulting pulp stream at a pH of 7.0 is introduced into a primary refiner prior to being combined in a secondary refiner with a dilute hard wood pulp stream pH of 7.0.

The dilute hard wood pulp stream having a solids content of 4 to 5 percent and a pH of 10.5 is passed (including trim white water) to the suction side of a pulp pump at a rate of 900 GPM. To the dilute hard wood pulp (solids content 4 percent) in the downstream conduit from such pulp pump, there is added 3.1 pounds per minute of gaseous carbon dioxide to form the dilute hard wood pulp stream at a pH of 7.0 introduced into the secondary refiner. From the secondary refiner the combined pulp stream is further diluted with white water (recovered from the wire pit of the paper machine and acidified with sulfuric acid) to a solids content of 0.4 percent and a pH of about 4.5 before introduction into a primary headbox. To the primary headbox, there is added 13.5 pounds of alum per minute.

The top sheet for the paper board is produced from a dilute soft wood pulp stream of a solids content of 4 to 5 percent which is introduced (together with trim white water) into the suction side of a pulp pump at a rate of 650 GPM to form a dilute pulp stream having a solids content of 4 percent in the discharge conduit therefrom. To this dilute pulp stream there is added 2.6 pounds per minute of gaseous carbon dioxide to form a dilute pulp stream of pH 7.0 which is successively passed through a primary and a secondary refiner. The thus refined pulp stream (pH 7.0) is withdrawn from the secondary refiner and mixed with white water (recovered from the wire pit of the paper machine and acidified with sulfuric acid) for dilution to a further diluted pulp stream of a solids content of 0.4 percent and a pH of about 4.5 before introduction into the primary headbox together with alum at the rate of 2.1 pounds per minute.

The controlled introduction of gaseous carbon dioxide instead of sulfuric acid prior to the refining steps eliminates certain dilution handling tanks and corrosive liquid piping. Additionally, the physical

properties of the resulting paper product are significantly improved because the easily regulating quantity and the self-buffering capabilities of gaseous carbon dioxide substantially eliminate pulp pH variations which can decrease paper strength.

### Example III

In a plant producing 1400 tons per day of paper, a concentrated pulp stream of pH of 11.0 and a density of 15 percent solids produced by kraft processing of soft wood and hard wood, is diluted to a consistency of 4 to 5 percent solids and a resulting pH of 10.5. The diluted pulp stream is introduced into and passed (with trim dilution, as required) to the suction side of a pulp pump 20 at a rate of 2000 GPM. To the dilute pulp stream in the downstream pipe 26 from the pulp pump, there is added gaseous carbon dioxide at a rate of 3.3 pounds per minute to form a dilute pulp stream having a pH of 8.0 when introduced into a refiner 28 for processing.

Additional gaseous carbon dioxide is added at a rate of 1.4 pounds per minute to the refined pulp in line 30 downstream from the refiner to form a combined stream in pipe 62 having a pH of 5.5.

Alum is added to the refined pulp stream at a rate of 6.7 pounds per minute. The thus treated refined pulp stream is thereupon further diluted with white water to a solids content of 0.4 percent and a pH of about 5.0 before introduction into the headbox 12 of the Fourdrinier machine 10 for processing into paper. No sulfuric acid is used.

In accordance with the process of the present invention, chemical cost savings are realized through elimination of about twenty pounds per ton of sulfuric acid resulting from the use of gaseous carbon dioxide to effect reduction of the pH of the raw and refined pulp. Further cost savings are sometimes possible because of the cost differential between carbon dioxide and sulfuric acid. Additionally, a reduction in rejected paper is realized by the process of the present invention.

In the preferred process, the use of sulfuric acid is eliminated, and the amounts of gaseous carbon dioxide introduced into the raw and refined pulp stream are individually selected to obtain optimum operation of the refiner 28 and the paper making machine 10. In order to optimize the refining process, the pH of the pulp stream in line 26 before the refiner is preferably in the range from about 8.5 to about 7.5. The pH of the white water 40 in the wire pit 42 of a paper making assembly is usually in the range 7.0 to 4.5, typically between 5.5 and 4.5. For this reason, the pH of the pulp stream in line 62 following the refiner is preferably in the range from about 6.0 to about 5.5. The use

of carbon dioxide to lower the pH of a combined stream to a value less than about 5.5 is usually uneconomical because increasing amounts of carbon dioxide are required.

Displacing sulfuric acid produces a paper sheet having a higher brightness. Still further, improved operation of the Fourdrinier machine is realized with improved effectiveness since pulp handling is effected in the absence of sulfuric acid and its corrosive effects.

The use of gaseous carbon dioxide significantly reduces the build up of barium sulfate (barium is present in the cellulosic raw material) and concomitant scaling of the paper making assembly therewith, thereby reducing the frequency of "boil-out" protocols which temporarily shut down the paper-making line.

The use of gaseous carbon dioxide in processing of recycled paper products has significantly improved the operation of the paper machines and associated equipment.

Numerous modifications and variations of the present invention are possible in light of the above teachings and therefore, within the scope of the appended claims, the invention may be practiced otherwise than as particularly described.

#### Claims

1. A process for manufacturing paper from alkaline cellulosic pulp produced by the delignification of cellulosic material wherein thus produced alkaline delignified cellulosic pulp is fibrillated in a refiner to form paper-forming pulp, characterised in that there is introduced into said delignified pulp gaseous carbon dioxide in an amount to form a precursor paper-forming pulp stream having a pH of from about 8.5 to about 6.5 prior to the fibrillation step.

2. A process according to Claim 1, wherein carbon dioxide is added in an amount to adjust the pH of said precursor paper-forming pulp stream to a value in the range from about 8.5 to about 7.5

3. A process according to Claim 1 or Claim 2, wherein a liquid stream obtained from a paper making operation is mixed with said delignified cellulosic pulp to form said paper-forming pulp to be contacted with said gaseous carbon dioxide.

4. A process according to Claim 3, wherein said liquid stream is mixed with said delignified cellulosic pulp and is introduced into a suction side of a pulp pump and wherein gaseous carbon dioxide is introduced into said paper forming pulp discharged from said pulp pump.

5. A process according to any preceding claim, wherein the pH of said paper-forming pulp stream is sensed to regulate the introduction of said gaseous carbon dioxide into said paper-forming pulp.

6. A process according to Claim 5, wherein pH is sensed prior to introduction of said paper-forming pulp stream into the refiner.

7. A process according to any preceding claim, further characterised in that there is introduced into the fibrillated pulp gaseous carbon dioxide in an amount to form a precursor paper forming pulp stream having a pH of from about 7.0 to about 5.5.

8. A process according to Claim 7, wherein the gaseous carbon dioxide is added to the fibrillated pulp in an amount to adjust the pH of said precursor paper forming pulp stream to a value in the range from about 8.0 to about 5.5.

9. A process according to any preceding claim, further comprising mixing a liquid stream obtained from a paper making operation with the stream of fibrillated pulp after it has been contacted with gaseous carbon dioxide.

10. A process according to any of Claims 7 to 9, wherein the pH of the stream of fibrillated pulp is sensed prior to the mixing step.

11. A process according to any preceding claim, in which no sulphuric acid is added to the alkaline cellulosic pulp.

12. An apparatus for manufacturing paper wherein delignified cellulosic pulp is fibrillated in a refiner to form paper-making pulp, characterised in that the apparatus includes means for injecting and dispersing gaseous carbon dioxide into a delignified cellulosic pulp stream in an amount to form a precursor paper-forming pulp stream having a pH of from about 8.5 to about 6.5 upstream from the refiner.

13. Apparatus according to claim 12 further including means for sensing the pH of said paper-forming pulp stream and regulating the introduction of carbon dioxide in response so as to maintain a desired pH.

14. Apparatus according to claim 12 or Claim 13, further including means for injecting and dispersing gaseous carbon dioxide into a fibrillated cellulosic pulp stream in an amount to form a precursor paper-forming pulp stream having a pH of from about 7.0 to about 5.5 downstream from the refiner.

15. Apparatus according to claim 14, further including means for sensing the pH of said precursor paper-forming pulp stream both upstream and downstream from the refiner and for regulating the introduction of carbon dioxide in response so as to maintain a desired pH both upstream and downstream of the refiner.

